

# PATENT SPECIFICATION

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NO DRAWINGS.

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## COMPLETE SPECIFICATION.

### Process for Preparing Alkaline Earth Metal Sulphonates from Alkyl Aromatic Sulphonic Acids.

We, ESSO STANDARD SOCIETE ANONYME FRANCAISE, a body Corporate organised under the laws of France, having an office at 6 Avenue Gambetta, Courbevoie (Hauts-de-Seine), France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns a process for preparing alkaline-earth metal sulphonates from sulphonic acids with unbranched aliphatic chains.

The manufacture of alkaline earth metal sulphonates, in particular calcium sulphonates, which are soluble in oil and used as detergents additives in motor oils is well known. However, whatever the origin of these sulphonates, whether natural sulphonates derived from the sulphonation of mineral oils or synthetic sulphonates derived from the sulphonation of the alkylation product of an aromatic compound by an olefine, they all have a common structural characteristic, viz. that the aliphatic chain or chains substituted on the aromatic nucleus are always highly branched. In this case, the obtaining of alkaline-earth metal sulphonates is easy and the product obtained on concentrating 40% by weight pure soap generally has a mean viscosity in the region of 30 to 50 cSt at 90°C, which makes for ease of handling.

It is moreover well known that to avoid having too viscous products it is possible, for instance in the case of the sulphonic acids obtained by treating mineral oils with oleum, to neutralise these acids with a base of an alkaline-earth metal in the presence of a small quantity of alkaline-earth metal chloride and if necessary, water.

However, the alkaline earth metal sulphonates in which the aliphatic chain has an unbranched structure have far too high a viscosity, for the usual concentrations in the region of 40% by weight pure soap; they are often unfilterable and most of the time have a tridimensional, birefringent structure relating them to gels.

The applicants have discovered that it is possible to prepare alkaline earth metal sulphonates of suitable viscosity from sulphonic acids of unbranched aliphatic chain type (preferably dissolved in a mineral oil), by effecting the neutralisation of these acids with an oxide or a hydroxide of an alkaline earth metal in the presence of 0.5 to 1.0% by weight based on the total weight of sulphonic acid and (if used) mineral oil, of a halide of that metal and an anhydrous low molecular weight aliphatic alcohol (as hereinafter defined).

By unbranched aliphatic chains are meant those which have branching for every other carbon atom as a maximum.

By low molecular weight aliphatic alcohols, are meant all the water-soluble alcohols, up to and including the C<sub>5</sub> alcohols; however, for preference methanol is used which, in particular, has the advantage of boiling at 65°C, so that by heating with reflux, the operation is automatically performed at a temperature entailing no risk of decomposing the sulphonated products.

The preferred alkaline-earth metal is calcium, and the preferred halide is chloride.

Alcohol will be used, preferably in a proportion of 10 to 50% by weight, and particularly 20 to 30% by weight based on the total weight of sulphonic acid and where used the mineral oil in which the acid is dissolved.

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The percentage of halide, e.g. chloride, of alkaline earth metal in relation to the total weight of sulphonate acid and (where used) mineral oil (but not alcohol) will be in the region of 0.5 to 1.0% by weight, and the higher it is the less branched will be the aliphatic chain.

The sulphonates with unbranched aliphatic chains, obtained by the process according to the invention, furnish better results than the alkaline earth metal sulphonates with highly branched chains.

The following example which is given by way of illustration and in no sense restrictive will better show the scope and importance of the invention.

#### EXAMPLE

A synthetic sulphonate acid obtained under the following conditions was treated:

In a continuous sulphonation apparatus, there was treated an aromatic hydrocarbon obtained by alkylating benzene with a propylene polymer prepared under pressure in

the presence of  $\text{BF}_3$ ; this aromatic hydrocarbon had a molecular weight of about 400. The delivery of alkylate was 2.5 l/h. At the same time, liquid  $\text{SO}_2$  was injected with a delivery of 2.5 l/h and liquid  $\text{SO}_3$  with a delivery of 0.244 l/h. Sulphonation was performed at  $-10^\circ\text{C}$ . The crude sulphonate acid obtained was freed from its solvent, diluted in 100% by weight of hexane and the decantation of the residue was carried out. The decanted solution was washed thrice with the aid of hydrochloric acid of density 1.19 to eliminate the sulphuric acid. The purified sulphonate acid was freed from its solvent by distillation in a partial vacuum and diluted with a suitable quantity of oil to bring its content of active matter to the desired proportion.

To obtain a calcium sulphonate, this acid was subjected to the treatment according to the invention and to two control treatments, by neutralising with lime in the presence of  $\text{CaCl}_2$ .

	Reactants	Treatment according to the invention		Control Treatments	
				1	2
50	Sulphonic acid at 40% by weight active matter	...	...	200	200
	Water	...	g	—	20
	Methyl alcohol	...	g	50	—
	$\text{CaCl}_2$	...	g	1	2
55	$\text{Ca}(\text{OH})_2$	...	g	18	18

In all cases, neutralisation is carried out by placing all the reagents in a flask fitted with a stirring device. Heating with reflux of water or methanol, as the case may be, is carried out for 2 hours. Finally, it is heated to  $150^\circ\text{C}$  to eliminate the water and

methanol. The product obtained is filtered at  $100^\circ\text{C}$  on a Buchner with the aid of 1% Supercel (a registered Trade Mark). Products having the following characteristics were obtained.

	Properties	Treatment according to the invention		Control Treatments	
				1	2
70	Cl wt. %	...	0.23	0.5	0.22
	Viscosity cSt at $99^\circ\text{C}$	...	33.7	41.6	144.6
	Alkalinity (1)	...	14	4	4
	Ca wt. %	...	2.15	2	1.90
	Colour ASTM (2)	...	2	3½	3½

(1) expressed in mg KOH per gram of product.  
(2) with 7% by weight active matter in a white oil.

It will be seen that in the case of the final viscosity being satisfactory, the use of methanol in place of water makes it possible to use half as much  $\text{CaCl}_2$ . It follows that the final product contains twice as much less

chlorine, which entails far less corrosion. Furthermore, the use of methanol enables additives to be obtained having a greater reserve of alkalinity, 14 instead of 4, which is of very great interest, since when these

oils are used in internal combustion engines, they are far better able to neutralise the acid residues.

WHAT WE CLAIM IS:—

- 5      1. A process for making alkaline earth metal sulphonates from alkyl aromatic sulphonlic acids with unbranched aliphatic chains (as hereinbefore defined) in which the sulphonlic acid optionally dissolved in a mineral oil is neutralised with an oxide or hydroxide of an alkaline earth metal, in the presence of 0.5 to 1.0% by weight of the total weight of sulphonlic acid and (where used) mineral oil of a halide of that metal 10      15 and an anhydrous low molecular weight aliphatic alcohol (as hereinbefore defined).  
2. A process as claimed in claim 1 wherein the low molecular weight aliphatic alcohol is methanol.  
20      3. A process as claimed in either of claims 1 and 2 wherein the alkaline earth metal is calcium.
4. A process as claimed in any one of the preceding claims wherein the proportion of alcohol is from 10 to 50% by weight based on the total weight of the sulphonlic acid and where used the mineral oil in which the acid is dissolved. 25
5. A process as claimed in claim 4 wherein the proportion is 20 to 30% by weight. 30
6. A process as claimed in any one of the preceding claims wherein the halide is a chloride. 35
7. A process as claimed in claim 1 substantially as hereinbefore described with reference to the Example.
8. Alkaline earth metal sulphonates obtained by a process as claimed in any one of the preceding claims. 40

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